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NITROGEN REMOVAL BY AMMONIA STRIPPING

Thomas P. O'Farrell, et al

District of Columbia Department of
Environmental Services

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Ammonia removals of up to 90% from lime clarified filtered wastewater were obtained in a five stage counter current cross flow stripping tower using air to liquid rates of 400 to 500 ft^3/gal. Decreases in operating temperatures from 78°F to 43°F during the cold weather reduced the stripping efficiency by 30% and caused icing in the tower. The variation of stripping efficiency was also studied as a function of the inlet pH of the water and the ratio of the air to liquid rate. The rate of calcium carbonate scaling on the tower was determined for wastewater pH's of 11.5 and 10.5. The heights of transfer units (HTU) were estimated by using a mathematical model and a computer iterative technique. (EPA)

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NITROGEN REMOVAL BY AMMONIA STRIPPING

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ABSTRACT

Ammonia removals of up to 90% from lime clarified filtered wastewater were obtained in a five stage counter current cross flow stripping tower using air to liquid rates of 400 to 500 ft^3/gal. Decreases in operating temperatures from 78°F to 43°F during the cold weather reduced the stripping efficiency by 30% and caused icing in the tower. The variation of stripping efficiency was also studied as a function of the inlet pH of the water and the ratio of the air to liquid rate. The rate of calcium carbonate scaling on the tower was determined for wastewater pH's of 11.5 and 10.5. The heights of transfer units (HTU) were estimated by using a mathematical model and a computer iterative technique.

This report is submitted in partial fulfillment of Project 11010 EYM and Contract No. 14-12-818 by the Department of Environmental Services, Government of the District of Columbia under the sponsorship of the Office of Research and Monitoring, Environmental Protection Agency. Work was completed as of October 1971.

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ACKNOWLEDGMENTS

The ammonia stripping tower was constructed by the Marley Company of Kansas City, Missouri. The system was constructed and operated by the staff of the EPA-DC Pilot Plant under the direction of Robert Hallbrook, chief mechanic; Walter Schuk, chief instrument technician and George Gray, chief operator.

Special data collection was conducted by F.P. Frauson, chemical engineer. The height of unit transfer was determined from the data by J.F. Roesler, sanitary engineer.

SECTION 1

CONCLUSIONS

1. Air stripping of ammonia in crossflow cooling towers with water temperatures of 80°F removed 90% of the ammonia from a non-nitrified lime clarified secondary effluent at pH 11.5 with an air to liquid rate of 500 ft^3 air/gallon liquid.

2. At an inlet water temperature of 77°F and an air to liquid rate of 327 ft^3 air/gallon liquid, efficiencies of ammonia removal at pH's 11.7, 10.5, and 9.7 were 86.2, 80.2 and 51.8%, respectively.

3. At pH 11.5, heavy calcium carbonate scale was produced within the stripping tower from the CO_2 in the air as the amount of excess calcium removed from the water was approximately 125 mg/l as $CaCO_3$. The scale reduced air rates which lowered the efficiency of ammonia removal. In addition, the scale was very hard. Because it could not easily be removed, it caused severe maintenance problems.

4. At pH 10.5 with a reduced calcium ion concentration the rate of calcium carbonate scale was reduced to 16 mg/l $CaCO_3$.

5. The efficiency of the tower for ammonia removal depended upon air temperature. A decrease in air temperature from 80°F to 43°F, reduced the efficiency of ammonia removal by approximately 30% for air to liquid rates from 100 to 500 ft^3 air/gallon liquid.

6. Freezing occurred when the wet bulb temperature within the tower reached 32°F, and produced a shut-down of the system.

7. The height of a transfer unit was developed and is described in the following equation.

$$HTU = K \left(\frac{G}{L}\right) 1.322$$

HTU = Height of Transfer Unit, ft.

G = Air Rate, lbs. moles/hr./ft^2.

L = Liquid Rate, lbs. moles/hr./ft^2.

K = 2.929 ft.

SECTION II

RECOMMENDATIONS

The use of air stripping for ammonia removal requires warm climates or summertime operation, a high lime process, and a low nitrate or non-nitrified wastewater. Because of these requirements the use of ammonia stripping within the USA as a means of continuous ammonia nitrogen removal is limited.

Where conditions permit the use of air stripping, additional studies are necessary to determine local scaling characteristics.

While calcium carbonate scale can be reduced by stripping the recarbonated effluent at pH 10.5 it probably can not be eliminated.

Thus future work should aim at developing suitable contacting systems to improve the mass transfer efficiency and to allow easy cleaning of the calcium carbonate scale. As an alternate approach, a search for chemical inhibitors to prevent the formation of calcium carbonate scale could also be performed.

SECTION III

INTRODUCTION

In raw wastewater and in effluents from secondary treatment plants without nitrification, ammonia, produced by enzymatic action on the waste product urea, accounts for approximately 90% of the total soluble nitrogen concentration. The remaining soluble nitrogen and all of the insoluble nitrogen are combined with organic compounds. Most of the ammonia may be removed from the wastewater by air stripping (1). A high pH is needed for efficient stripping and is achieved by combining the stripping process with lime clarification (1). The addition of lime in the clarification of wastewater for phosphorus and solids removal increases the wastewater's pH and converts ammonium ion to ammonia as follows:

$$NH_4^+ + OH^- \rightleftharpoons NH_4OH \rightleftharpoons NH_3 + H_2O$$

Unfortunately, ammonia is highly soluble in water and its volatility decreases markedly with decreasing temperatures. For these reasons effective air stripping requires warm temperatures and the use of large volumes of air per gallon of water.

To reduce power requirements, cooling towers, which provide a low pressure drop, have been used for air stripping of ammonia at South Lake Tahoe (1) and Pretoria, South Africa (6). The ammonia removal efficiency of the system at South Lake Tahoe has been reduced both by low temperatures and $CaCO_3$ scaling. The low winter temperatures reduce the ammonia removal to less than 60% by decreasing the ammonia volatility and also by icing the tower. Calcium carbonate scale at Tahoe also increases the pressure drop through the tower reducing air rates and the stripping efficiency. In contrast, the warm climate in Pretoria, South Africa, eliminates the temperature problems for most of the year. Severe $CaCO_3$ scaling does not occur (7).

With the variation in the performance of air stripping systems, a pilot study was performed in the EPA-DC Pilot Plant to evaluate temperature, pH, and scaling in the stripping process, and to determine the mass transfer characteristics (height of the transfer unit) of a polypropylene grid packing in crossflow towers. The stripping process was included in a tertiary system (Figure 1) which consisted of lime precipitation, air stripping of ammonia, filtration, carbon adsorption, and solids handling.

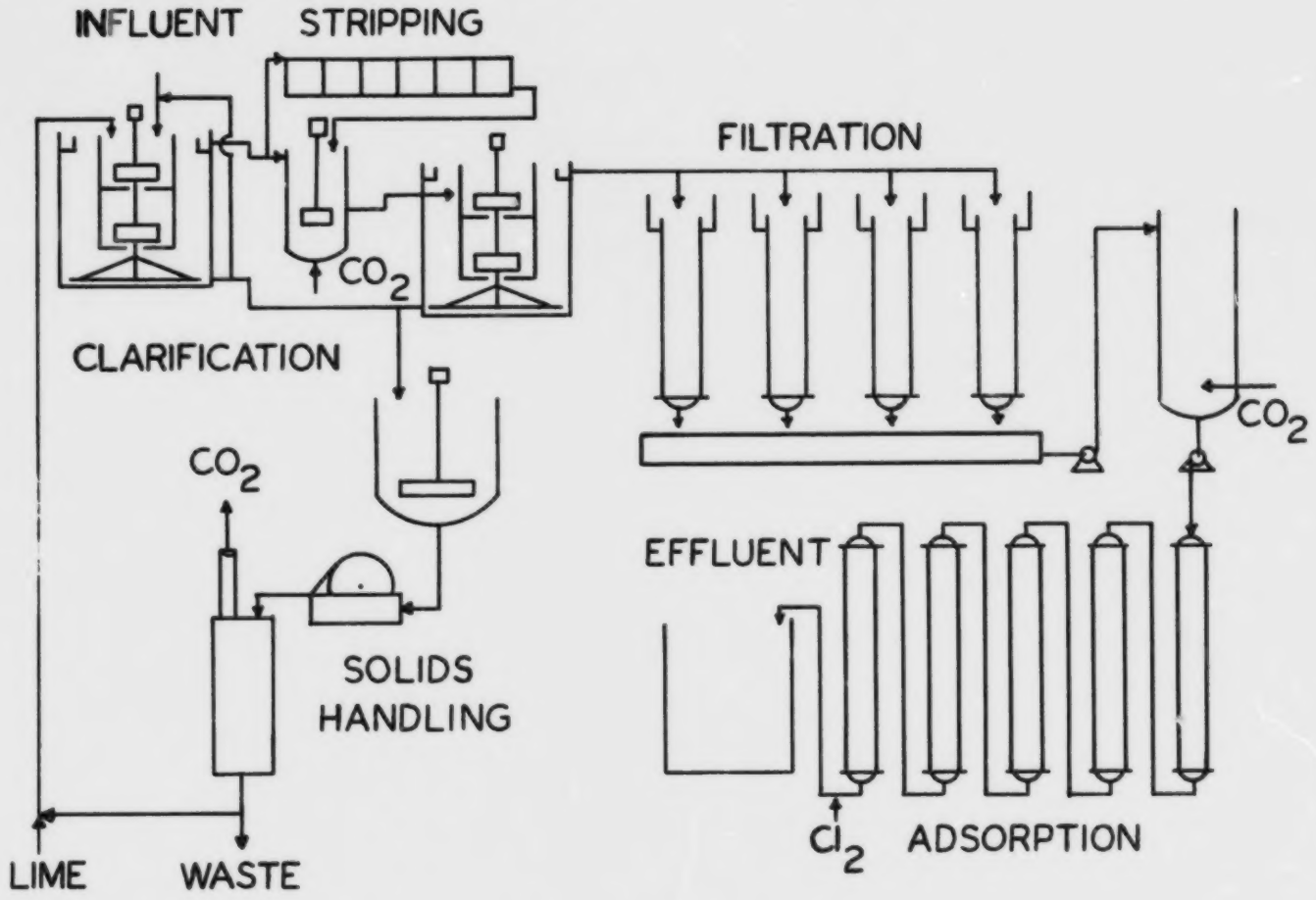

Figure 1. Advanced Waste Treatment Pilot Plant

SECTION IV

EXPERIMENTAL

In the stripping process (Figure 2), a series of five Marley crossflow cooling towers were each packed with forty, 4 ft. x 5 ft. x 1/2 inch polypropylene grids. The layers of each grid were spaced every 2 1/2 inches and the grids were packed to promote waved air flow through the system. The air was drawn through the towers by a 24-inch centrifugal fan operated by a 5-HP motor. The water was pumped to a distribution box located on the top of each tower and flowed downward over the grids. The water flow between towers was controlled by automatically maintaining a constant level in the collection basin of the preceding tower. The air was drawn countercurrent to the flow of water between towers and cross flow within the packing of each tower.

Two types of secondary effluents were fed to the (lime precipitation and ammonia stripping) treatment system: first, the effluent from the District of Columbia's Water Pollution Control Plant (modified aeration) and later, the effluent from the EPA-DC Pilot Plant step aeration process.

The District of Columbia's modified aeration system (270 MGD), with 2 hours of aeration time and 500 mg/l of mixed liquor suspended solids, never nitrified and approximately 12 mg/l of NH_3-N was available for air stripping. The EPA-DC Pilot plant's step aeration system (0.1 MGD), however, with 3.8 hours of aeration time and with 3000 to 4000 mg/l of mixed liquor suspended solids, produced nitrification in warm weather and reduced the available ammonia for air stripping. The quality of these effluents and the nitrogen contents are given in Table 1.

During the operation of the ammonia stripping process, lime precipitation, operated in two stages with intermediate recarbonation (Figure 3), included liming (300 to 400 mg/l as CaO) the water in the first stage reactor to produce a pH greater than 11.5, recarbonating with carbon dioxide to pH 10.5 for precipitation of the excess calcium ions, and finally flocculating and clarifying the precipitated calcium carbonate in a reactor identical to the first stage reactor. The effluent from either the first (pH 11.5) or the second (pH 10.5) stage clarifier (Figure 3) was fed to the stripping system. In the temperature study, the system was operated at various air to liquid rates (G'/L') during periods of warm and cold temperatures. Liquid loading rates were varied from 1.0 to 2.44 gpm/ft^2. Air rates were varied from 100 to 750 ft^3 air/gallon liquid by a damper setting. With the available capacity of the fan, G'/L' rates of greater than 400 ft^3 air/gallon liquid could be achieved only at a liquid loading rate of 1 gpm/ft^2.

In the pH study, influent wastewater at pH's 11.7, 11.3, 10.5

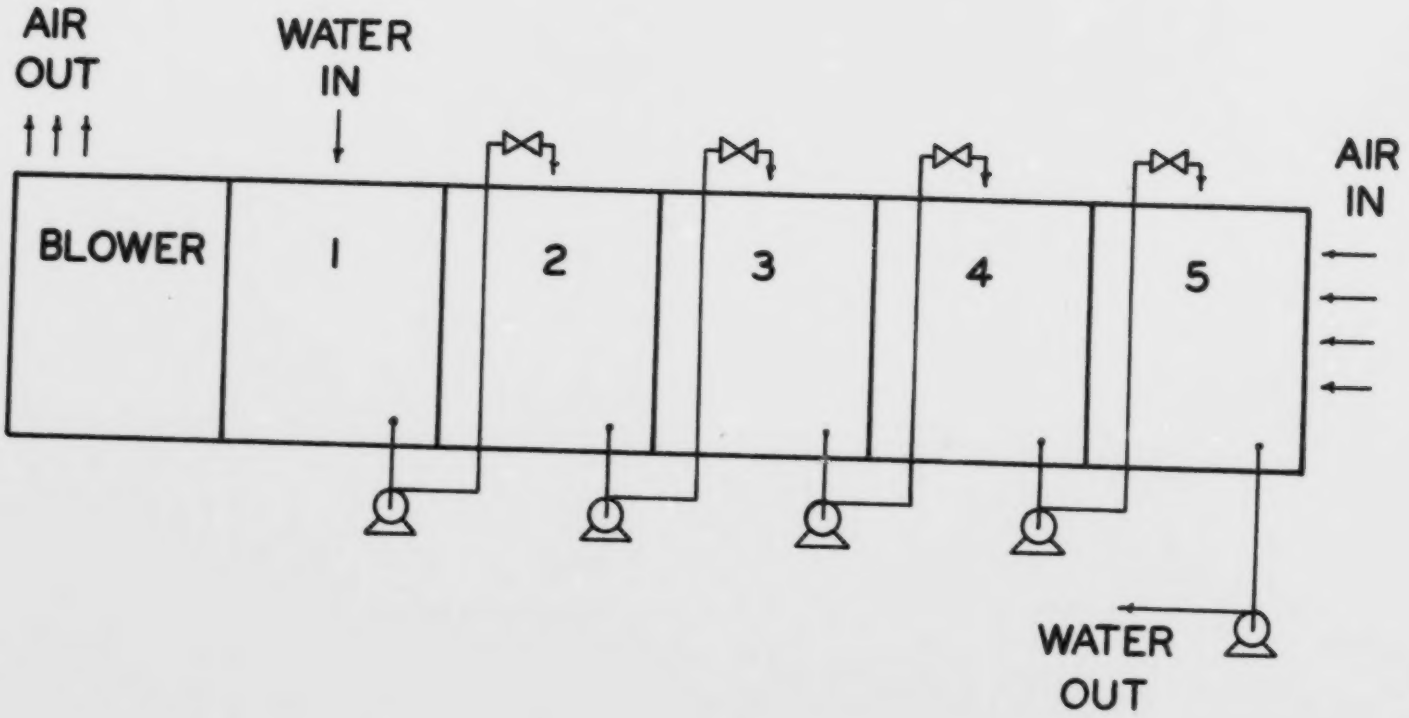

Figure 2. Ammonia Strippers

TABLE 1

SECONDARY EFFLUENT CHARACTERISTICS

EFFLUENT	BOD mg/l	SUSPENDED SOLIDS mg/l	TKN-N mg/l	NH_3-N mg/l	$(NO_3 + NO_2)$-N mg/l
District of Columbia (modified)	48.0	68	20.4	12.0	0.14
EPA-DC (Step non-nitrified)	13.4	27	10.9	9.5	0.9
EPA-DC (Step nitrified)	20.7	44	5.3	2.0	10.0

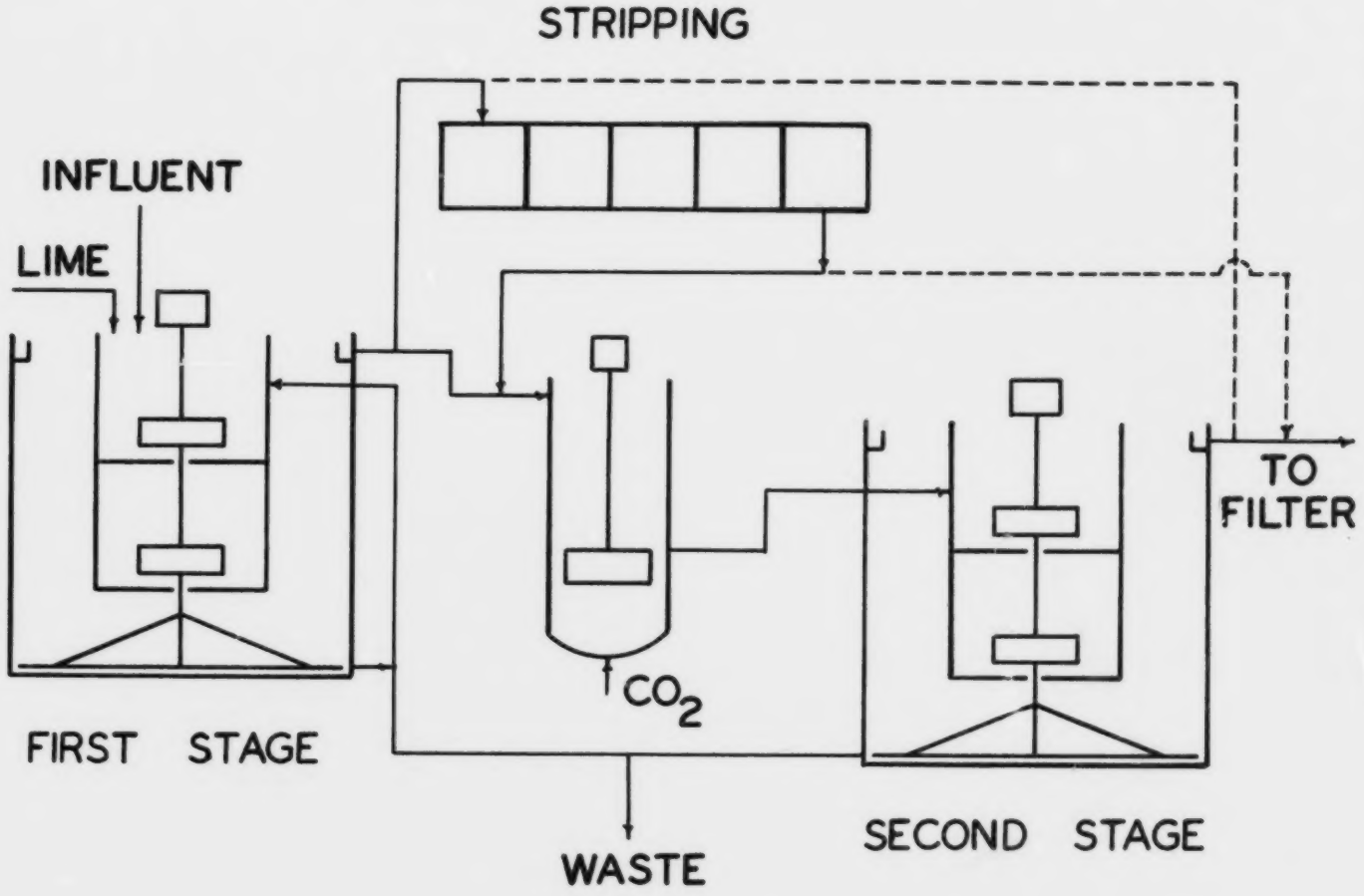

Figure 3. Lime Precipitation and Ammonia Stripping System

and 9.7 were fed to the tower at a liquid loading of 2 gpm/ft^2 (32 gpm) with an average air to liquid rate (G'/L') of 327 ft^3 air/gallon liquid. For an influent at pH 11.7, the system was fed effluent from the first stage chemical clarifier. Influents at pH's 11.3, 10.5, and 9.7 were provided from the second stage clarifier with the pH controlled by the appropriate addition of carbon dioxide in the recarbonation tank.

During the two continuous operations to determine the effect of scale, the influent to the system was continuously fed at pH 11.5 and later at pH 10.5 with a liquid loading rate of 2 gpm/ft^2. At both pH levels, the initial air to liquid rate was approximately 350 ft^3 air/gallon liquid.

The high pH scaling test was initiated in late July, 1969 on limed (D.C. modified aeration) effluent from the first stage lime clarifier which contained an excess calcium ion concentration of 150-200 mg/l Ca^{++}. The scaling test at pH 10.5 was initiated in late March 1970 and continued into mid July 1970 on limed (Pilot Plant step aeration) effluent from the second stage lime clarifier with inlet calcium ion concentrations of approximately 50 mg/l Ca^{++}.

During both the temperature and pH studies, liquid samples of the influent and effluent from each tower were analyzed for ammonia, calcium, temperature, pH and alkalinity. The relative humidity of the influent air and the temperature of the air between each stage were also recorded. The ammonia concentrations were determined by an automated Technicon procedure (2). The calcium concentrations were determined on a Perkin-Elmer Model 303 Atomic Adsorption Spectrophotometer. The alkalinities were determined by the procedure in Standard Methods (5).

SECTION V

TEMPERATURE EFFECTS

In warm weather tests at pH 11.5 with inlet air and water temperatures averaging 78 and 79°F, respectively, air stripping cooled the outlet water temperature by evaporation of the liquid within the tower to an average of 72°F. In a similar test with the inlet air temperature averaging 43°F and the inlet water temperature averaging 61°F, the air stripping cooled the outlet water to an average temperature of 41°F.

The efficiency of the tower (Figure 4) for ammonia removal was directly dependent upon the air and water temperature. The efficiency of the system during the warm weather tests increased from 50% at 100 ft^3 air/gallon liquid to 90% at approximately 500 ft^3 air/gallon liquid. During the cold weather tests, however, the removal efficiency increased from 20% at 100 ft^3 air/gallon liquid to 60% at 500 ft^3 air/gallon liquid. The decrease in efficiency from the warm to cold temperatures was approximately 30% over the entire air to water flow range. In addition to the decreased stripping efficiency, tower operation was also interrupted by icing. Since the ammonia stripping system is an efficient cooling tower, evaporation within the tower cooled the outlet water and air temperatures. Thus, icing within the tower occurred when the wet bulb temperature of the air within the tower reached 32°F even at inlet air temperatures greater than 32°F.

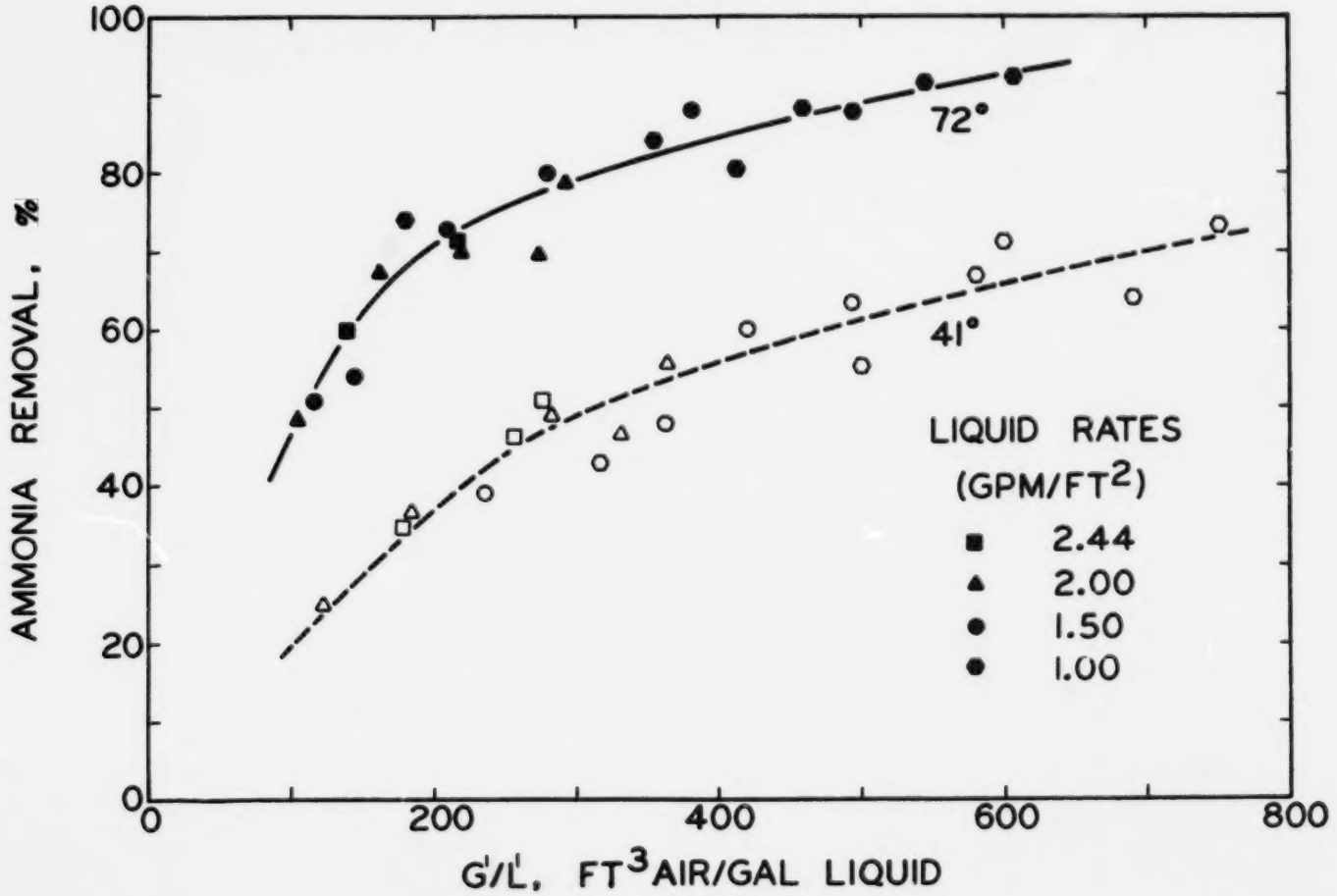

Figure 4. Effect of Temperature on Ammonia Removal Efficiency

SECTION VI

pH EFFECTS

The effect of influent pH on the removal efficiency of ammonia was determined during the summer with the inlet water and air temperatures averaging 77 and 76°F, respectively. During air stripping, the water was cooled to an average outlet water temperature of 69°F. The results of air stripping through various packing depths with influents at pH's 9.7, 10.5, 11.3, and 11.7 are shown in Figure 5. As seen, the efficiency of removal was dependent upon pH with the highest removal (86.2%) obtained at pH 11.7. However, the decrease in efficiency of removal from pH 11.7 to 10.5 was approximately 6%. The decrease in inlet pH from 11.7 to 9.7, however, produced a marked decrease in total efficiency from 86.2 to 51.8%.

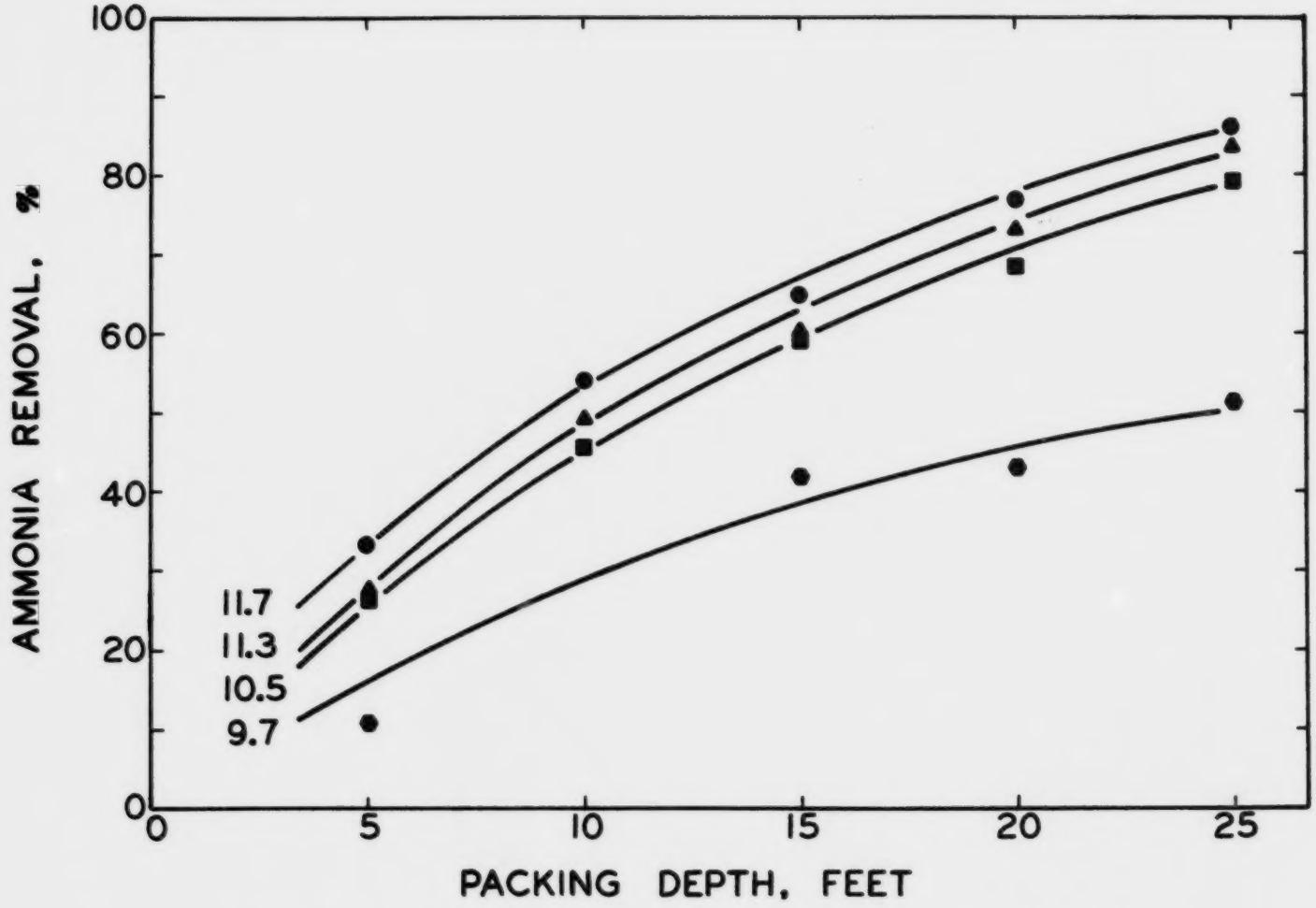

Figure 5. Effect of pH on Ammonia Removal Efficiency

SECTION VII

SCALING EFFECTS

The system was operated with the influent at a pH greater than 11.5 for 75 days. During the operation, the inlet ammonia concentration averaged 11.5 mg/l NH_3-N. The efficiency of the system (Figure 6) decreased from 80 to 55% (residual NH_3-N = 2.5 to 4.5 mg/l) over the 75 days as the formation of $CaCO_3$ scale in the tower decreased the air to liquid (G'/L') rates from an initial 350 ft^3 air/gallon liquid to 250 ft^3 air/gallon liquid. Near the end of the 75 days of operation, the efficiency of the system, however, had decreased by approximately 20% more than that expected for the decrease in the G'/L' at an average air temperature of 78°F (Figure 4). The additional loss of efficiency was produced by a decrease in ambient air temperature from 80°F to 59°F.

The accumulation of calcium carbonate scale within the connecting pipes and control valves forced intermittent shut-down of the system for maintenance. At the end of the high pH ($\sim$11.5) operation, the towers were opened for inspection. A heavy scale of calcium carbonate was evenly distributed throughout the towers, while negligible scaling occurred in the distribution box of the first tower and associated inlet piping. Thus, the scaling was not caused by post precipitation of the effluent from the first-stage clarifier but by the formation of calcium carbonate from the carbon dioxide in the stripping air.

The average packing grid increased from a tare weight of 2 lbs. to 22 lbs. or by 20 lbs. of calcium carbonate scale. The scale, 1/4 to 3/8 inches thick, contained more than 99% calcium carbonate with traces of organic carbon and phosphorus. The scale was crystalline, hard, and could not be removed by a high pressure water hose. Each grid had to be manually cleaned. With forty grids per tower, the total accumulation of scale in the five towers was approximately 4000 lbs. Based on the accumulated flow through the system, the 2 tons of scale corresponded to a scale rate of 125 mg/l of calcium carbonate. Material balances with alkalinity analyses verified this result.

In addition to the effect of calcium carbonate scaling on maintenance and reduction in air capacity, the loss of the calcium carbonate seriously affected the operation of the chemical clarification system on the D.C. modified secondary effluent. Control of the slurry pool in the first clarifier (3) required recycle of the solids from the second-stage clarifier to the first. Since 35% of the calcium carbonate was lost through scale formation in the stripping tower, the calcium carbonate produced in the recarbonation process and recycled to the first-stage clarifier was not sufficient to stabilize the slurry pool in the first-stage lime clarifier. Hence, periodic overflow of the solids into the ammonia stripping system also interrupted the stripping process.

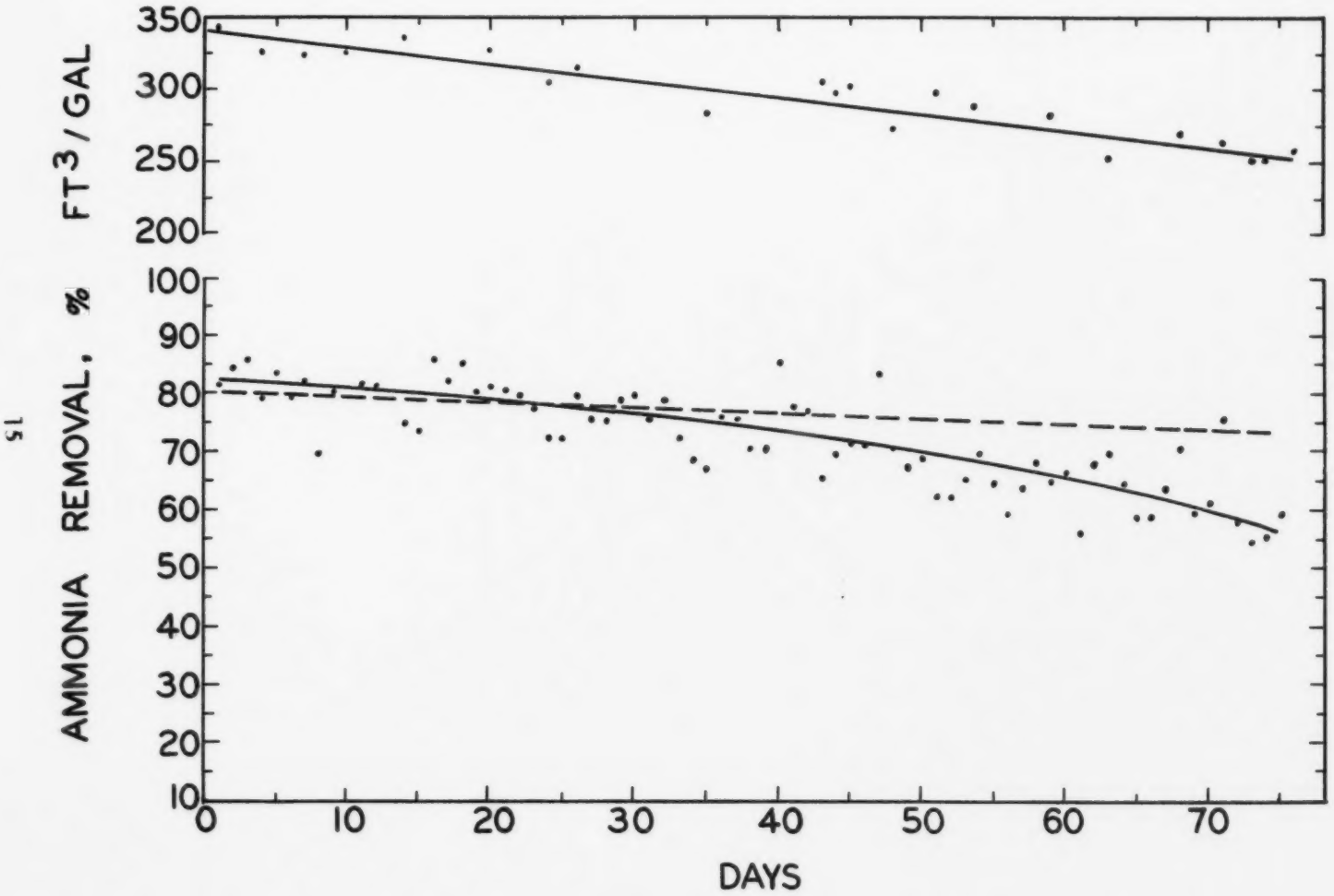

Figure 6. Continuous Operation at pH 11.5

In the low pH (10.5) operation, the influent to the tertiary treatment system (chemical clarification and ammonia stripping) was the effluent from the EPA-DC Pilot Plant's secondary (step aeration) treatment system. The step aeration process fluctuated through various stages of nitrification, and thus after chemical clarification provided an influent of varying ammonia concentration to the ammonia stripping column (Figure 7). During the first seventeen days of operation (Figure 7), nitrification did not occur in step aeration. The average concentration of ammonia in the inlet and outlet of the tower were 9.5 and 4.2 mg/l NH_3-N, respectively, for an average removal of 56%. During this period, the average outlet water temperature was 45°F with an average G'/L' value of 347 ft^3 air/gallon liquid. Between the 35th and 45th day of operation, the step aeration system produced little nitrification and the percent removal of ammonia averaged 66% (3.1 mg/l NH_3-N average residual) with an average outlet water temperature of 57°F. During the pH studies, nearly 80% of the ammonia was removed under similar operating conditions with an outlet water temperature of 69°F.

While stripping efficiencies were affected by nitrification, the rate of calcium carbonate scaling and its effect upon the reduction in the air to liquid ratio were unaffected. The calcium carbonate scale in the pH 10.5 tests reduced the air to liquid ratio from an initial 350 ft^3 air/gallon liquid to approximately 330 ft^3 air/gallon liquid (Figure 8) over the 112 day period. During this period, the inlet and outlet calcium ion concentrations averaged 48.3 and 41.8 mg/l of Ca^{++}, respectively. The calcium ion decrease corresponded to a calcium carbonate scaling rate of 16 mg/l $CaCO_3$.

It was hoped that operation at the lower pH would produce a softer scale which could be easily flushed from the packing. Examination of the scale showed it to be as hard as the scale formed at pH 11.5. Unfortunately, during this long-term test at low pH, several extended runs were made at pH 11.5. Consequently, a definitive statement cannot be made about the relative hardness of the scale at pH 10.5.

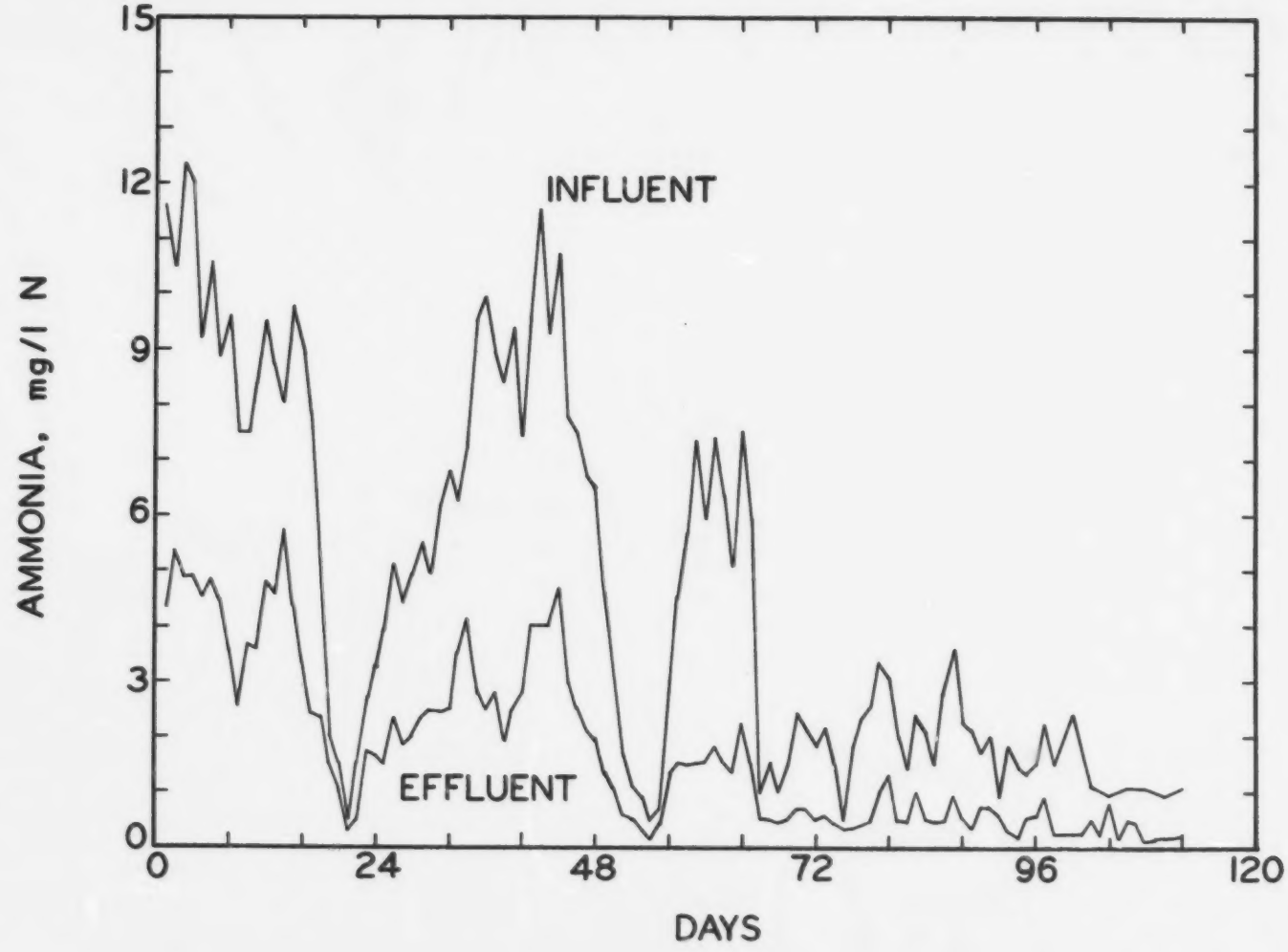

Figure 7. Effect of Nitrification on Ammonia Removal Efficiency

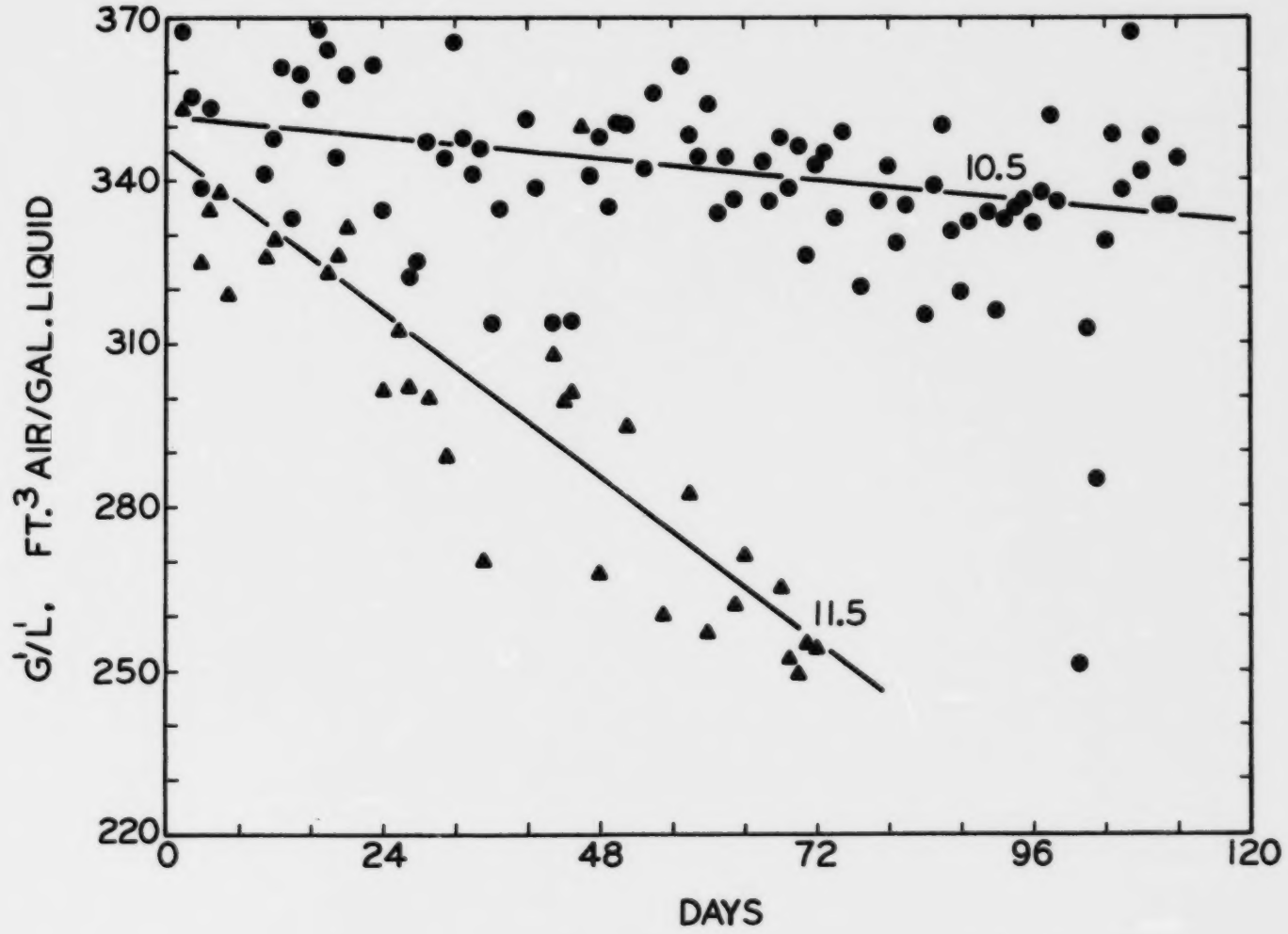

Figure 8. Effect of Scaling on Air Rate at pH 10.5 and 11.5.

SECTION VIII

TRANSFER COEFFICIENTS

A mass transfer correlation in crossflow cooling towers has been developed for air stripping of ammonia by Roesler et al. (4). The correlation employs an iterative computer procedure to determine the height of the transfer unit for the packing within the crossflow cooling tower. The procedure includes both temperature and humidity in the correlation.

The mass transfer characteristics of the tower were evaluated through the computer program. Data from fifteen controlled runs on the first crossflow tower with an influent pH of 11.7 and warm temperatures were used to calculate the overall gas height of a transfer unit (Figure 9). The data was collected over a three day period; thus changes in packing characteristics produced by a gradual increase in scale formation were minimal.

The equation from a least square regression of the data is:

$$HTU = K \left(\frac{G}{L}\right) 1.322$$

HTU = Height of Transfer Unit, ft.

G = Air Rate, lbs. moles/hr/ft^2

L = Liquid Rate, lbs. moles/hr/ft^2

K = 2.929 ft.

The regression yielded a correlation coefficient of 0.91.

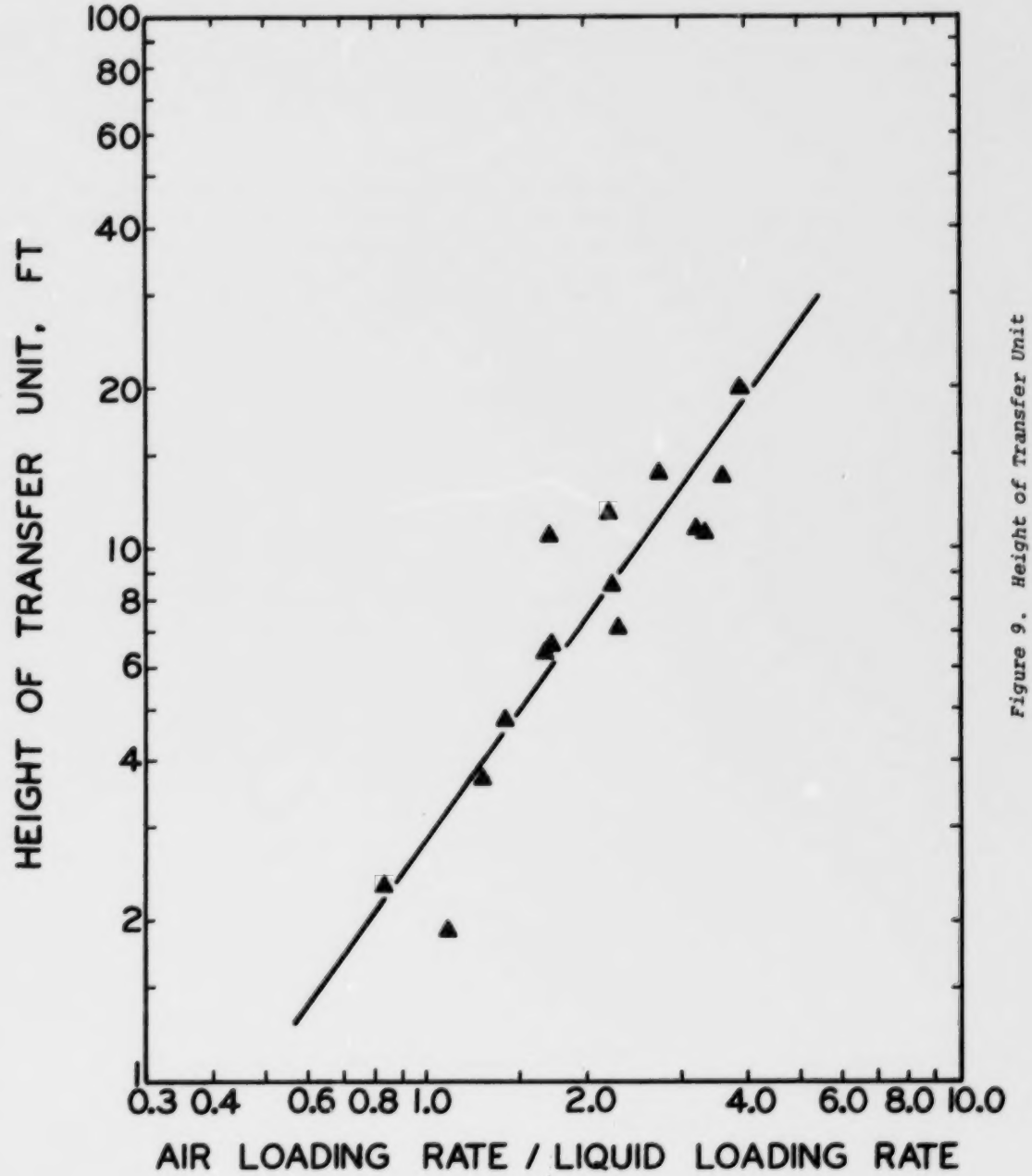

Figure 9. Height of Transfer Unit

SECTION IX

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SECTION X

PUBLICATIONS

O'Farrell, T.P., Frauson, F.P., Cassel, A.F., and Bishop, D.F., "Nitrogen Removal by Ammonia Stripping," presented at the 160th National ACS Meeting, Chicago (September 1970).

This paper has been accepted and will be published in the Journal of the Water Pollution Control Federation.

SECTION XI

GLOSSARY

Air Stripping - The transfer of the volatile component ammonia from water into air by physical contact of the water with air.

Ammonia-Nitrogen (NH_3-N) - The weight of ammonia expressed in terms of the nitrogen combined in ammonia, i.e. the weight of ammonia x $\frac{14.}{17.}$

Countercurrent Flow - With reference to the air water system, if the water flows from tower 1 to tower 6 in sequence, the air flowed from tower 6 to tower 1 also in sequence.

Cross Flow - Refers to the flow of air and water in the column. The water flowed from top to bottom and the air from one side across to the opposite side.

G'/L' - Ratio of air to water flow, ft^3 of air/gallon of water.

HTU - Height of a transfer Unit. In terms of a single length dimension, the height of apparatus required to accomplish a separation of standard difficulty.

MGD - Million gallons per day.

Mixed Liquor Volatile Suspended Solids - Approximation of the quantity of micro-organisms present in mg/l.

Modified Aeration - An activated sludge process typified by relatively low mixed liquor suspended solids, short detention time and high organic loading.

Step Aeration - An activated sludge process in which the wastewater is added at the 1/4, 1/2 and 3/4 points along the length of the reaction basin.

Nitrification - The biological conversion of ammonia under specific conditions to first nitrite and then nitrate.

Recarbonation - Removal of Ca^{++} from limed water by precipitation as $CaCO_3$, achieved by bubbling CO_2 through the water.